

Determination of Free Urea in Ethyl Stearate Adduct by X-Ray Diffraction

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► A method for the direct determination of free urea in urea adducts of ethyl stearate by x-ray diffraction was developed. Known amounts of the urea and urea-free ethyl stearate adducts were mixed as dry powders and pressed into disks. These disks were reground and repressed until random orientation was obtained. The ratio of the height of the 4.0 Å. peak of free-urea to that of the 4.1 Å. peak of the adduct was calculated by statistical methods for each mixture in the series. A graph of these ratios plotted against the per cent free urea was used as a standard curve for the determination of free urea in unknowns. Ethyl stearate was chosen only as a representative guest molecule for this study. In principle, this method should be applicable to any type of inclusion compound when host and adduct are crystalline solids.

SINCE THE DISCOVERY of urea adducts (1) in 1940 by Bengen, they have become the subject of much serious work. One of the chief difficulties in quantitative studies of the physical properties of these adducts is the presence of free urea in unknown amounts. Since the crystal structure of urea is different from that of its adducts (5), x-ray diffraction (3) can be used for estimating the amount of free urea. Herrmann (2) has used x-ray analysis for assaying the amount of adduct from the intensity of adduct diffraction maxima, with reference to a specimen presumed to be pure. This would be insufficiently sensitive to determine small quantities of free urea that would interfere with studies of physical properties, since urea would have to be determined by difference.

We have developed a method for direct determination of free urea from

the ratio of heights of a free urea maximum and an adduct maximum. In order to develop the details of the procedure, known amounts of urea and urea-free ethyl stearate adducts were mixed as dry powders and pressed into disks for x-ray examination.

EXPERIMENTAL

Preparation of Adduct. Following method 2 of Swern (7) 1 gram of ester was added to a solution of 5 grams of urea in 20 ml. of absolute methanol and 3 ml. of isopropanol. The mixture was heated until clear. The solution was allowed to cool to room temperature and the precipitate filtered off. The precipitate was washed three times with absolute methanol to dissolve any excess urea and three times with benzene to dissolve any excess ester. X-ray diffraction indicated that this washing procedure was adequate since 10-fold

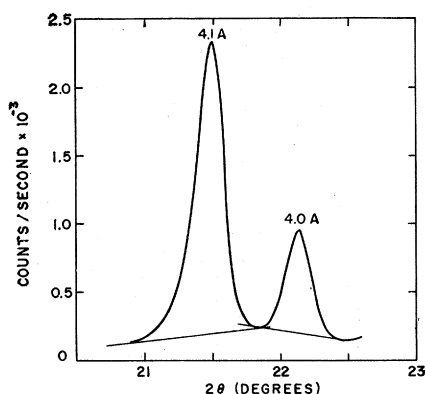


Figure 1. Diffracted height vs. 2θ angle showing method of choosing base lines

scale expansion revealed no evidence of uncomplexed materials.

Mixed Standard. A gravimetrically prepared mixture was ground in a ceramic mortar, mechanically mixed with a stirring rod, and molded at 20 tons per sq. inch for 5 minutes. After x-ray examination, the disk was reground, remolded, and re-examined by x-ray. This regrinding and molding procedure was repeated seven times for each ratio of excess urea to adduct. Disks were kept in a desiccator when not in use.

X-Ray Technique. X-ray diffraction measurements were made with a General Electric XRD-3 direct recording diffractometer, using nickel-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$), 1° beam slit, 0.1° detector slit, medium resolution Soller slit, 0.2° per minute scanning speed, 12 inches per hour chart speed, and 8-second time constant.

The heights of the diffraction maxima were measured as counts per second at the maximum minus counts per second of a base line determined by the procedure shown in Figure 1. Results were expressed as the ratio of corrected height of free-urea peak (4.0 Å.) divided by corrected height of adduct-peak (4.1 Å.). The region of interest (20° to 23° , 2θ) was rescanned for 6 different orientations of the sample disk, three on each side randomly chosen.

RESULTS AND DISCUSSION

The 4.0 Å. peak of free urea and the 4.1 Å. peak of the adduct were chosen for this study because they were very intense, close together in 2θ value, and far enough removed from other diffraction maxima that their heights could be measured without serious interference from other maxima. The d-spacing of the 4.1 Å. peak of the adduct is independent of the chain length of the guest molecule. The base line was taken as shown in Figure 1 because this method is rapid and reproducible.

The first disk pressed for each standard showed markedly different intensity ratios on opposite faces. Therefore, each disk was reground and repressed several times, x-ray measurements taken after each pressing. The average over

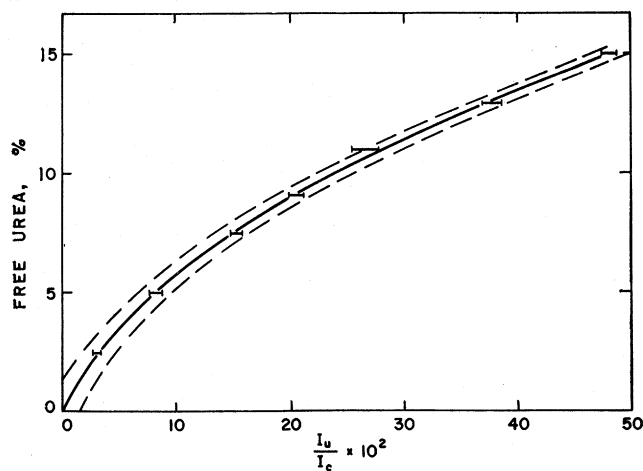


Figure 2. Relation between percentage of free urea and ratio of height at free urea maximum to height at adduct maximum

both sides of the disk also changed with regrinding for the first three grindings. However, a statistical analysis showed that the intensity ratio did not significantly vary from grinding 3 to grinding 7, and these were used in our calculations. This is similar to the experience of Meakins with dielectric measurements of pressed disks of mixed materials (4). Occasionally one of the grindings between 3 and 7 showed an average intensity ratio too far removed from the mean of the other regrindings and was omitted from the calculations. This could have been caused by small local concentrations of free urea oriented to give a strong 4.0 Å. reflection.

Our experience has been that the variation with regrinding was not observed with unknown mixed samples obtained by precipitation. Even the very first pressing showed essentially the same intensity ratio on each side of the disk, and the overall average for the disk did not vary significantly from grinding to grinding. This implies that regrinding and pressing seven times should only be necessary for mechanically mixed powders.

In Figure 2 the per cent free urea in the adduct of ethyl stearate is plotted against the average intensity ratio. The horizontal lines shown in Figure 2 are the 95% confidence limits of each average intensity ratio. The midpoint of each line is the average of 30 ratios: 5 disks (grindings 3 through 7), 6 orientations per disk. The dashed curves in Figure 2 represent 95% confidence limits, based on a pooled variance (6), obtained from

$$2.045 \sqrt{\frac{\sum_{i=1}^7 s_i^2}{7}}$$

where s_i^2 is the variance of each average intensity ratio. The curve is not linear (3) because of the way the base line was

taken but seems to approach linearity at higher values of free urea content.

In using this method a sample to be analyzed should be reground and repressed a few times as a means of checking whether regrinding is necessary to bring about random orientation. The average of the intensity ratios of those disks displaying random orientation is entered as the abscissa of the graph and the corresponding per cent free urea is read as the ordinate. Experience may later show that regrinding of precipitated samples is unnecessary.

Ethyl stearate was chosen only as a representative guest molecule for this study. In principle this method should be applicable to any type of inclusion compound where host and adduct are crystalline solids.

ACKNOWLEDGMENT

The authors gratefully acknowledge Joe N. Boyd of Biometrical Services of Agricultural Research Service for helpful suggestions concerning statistical analysis.

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RECEIVED for review September 8, 1964. Accepted November 30, 1964. Mention of commercial products does not constitute an endorsement by the United States Department of Agriculture over others of a similar nature not mentioned.